

PETROGRAPHIC AND GEOCHEMICAL ANATOMY OF LITHOTYPES FROM THE BLUE GEM COAL BED, SOUTHEASTERN KENTUCKY

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INTRODUCTION

The nature of the association of major, minor, and trace elements with coal has been the subject of intensive research by coal scientists (Swaine¹; and references cited therein). Density gradient centrifugation (DGC) offers a technique with which ultrafine coal particles can be partitioned into a density spectrum, portions of which represent nearly pure monomaceral concentrates. DGC has been typically conducted on demineralized coals² assuring, particularly at lower specific gravities, that the resulting DGC fractions would have very low ash contents.

In order to determine trends in elemental composition, particularly with a view towards maceral vs. mineral association, it is necessary to avoid demineralization. To this end the low-ash, low-sulfur Blue Gem coal bed (Middle Pennsylvanian Breathitt Formation) from Knox County, Kentucky, was selected for study. The objective of this study was to determine the petrography and chemistry, with particular emphasis on the ash geochemistry, of DGC separates of lithotypes of the Blue Gem coal bed.

EXPERIMENTAL

SAMPLE PREPARATION AND CHARACTERIZATION

Samples were obtained from the Blue Gem coal bed from a mine site in the Barbourville 7½ minute quadrangle, Knox County, Kentucky. The coal bed, 70 cm thick, was sampled in a series of five benches. Sample KCER-5447 represents the 10.0 cm basal bench of the coal bed. KCER-5445 represents an 11.6 cm lithotype from the middle of the coal bed.

Bench samples were crushed and split following procedures recommended by ASTM standard D2013.³

Proximate, ultimate, and sulfur analyses were determined for each bench sample according to standard ASTM techniques.³

Subsplittings of the -20 mesh coals were mixed with epoxy resin and prepared into pellets for petrographic analysis and polished according to standard procedures.⁴

DENSITY GRADIENT CENTRIFUGATION SEPARATION

Maceral separation was based on the DGC method developed by Dyrkacz and co-workers⁵⁻⁶ with certain modifications.² Additional modifications included omission of the demineralization step, crushing the feed coal to -325 mesh, and adding Brij-35 surfactant to the separation media (due to the smaller particle size) to suppress particle agglomeration.

PIXE ASH GEOCHEMISTRY

The major and minor element geochemistry of the high temperature ashes of all of the lithotypes, the whole coal samples of the three lithotypes subjected to DGC separation, and the "whole coal" DGC density fractions was determined using Proton Induced X-ray Emission (PIXE). Procedures for PIXE analysis can be found in Savage.⁷

X-ray fluorescence analysis of the lithotype high temperature ashes was conducted at the CAER using techniques described by Hower and Bland.⁸

RESULTS

PETROGRAPHIC ANALYSIS OF BENCH AND DGC SAMPLES

Petrographically, the bench samples have relatively high vitrinite contents, with samples containing between 77.6 and 87.3% vitrinite (Table 1). Coal rank is high volatile A bituminous (0.88% R_{max}). Petrography of the KCER-5445 DGC separates is given on Figure 1.

In the DGC fractions recovered between 1.25-1.30 g/mL, vitrinite content is over 90%. The partitioning of macerals into relatively pure fractions with little association of

mineral matter was therefore encouraging for the interpretations to be made in the accompanying geochemical studies.

In each study sample, there is an abrupt transition from vitrinite-dominated to semifusinite-dominated DGC fractions at about 1.30-1.31 g/mL and a similar, though less abrupt, transition from semifusinite- to fusinite-dominated fractions at about 1.33-1.34 g/mL. Mixed maceral fractions dominate the lower density range.

GEOCHEMICAL CHARACTERIZATION OF BENCH SAMPLES

Aside from the top bench of the coal bed, KCER-5443, which has an ash content of 9.15% and a total sulfur content of 2.32%, the coal is very low in ash (0.40 - 1.47%) and sulfur (less than 0.8%). Elemental analyses suggest the presence of clays (Si and Al), carbonates (Fe and Ca), and, in the upper bench, possibly pyrite (Fe and S). This is supported by previous observations on the mineralogy of this coal bed.⁹ Several trace elements are enriched in the center of the coal bed (Ba, Cu, Mo, and Sr); other elements (Cr, Co, Mn, V, Ti, and Zr) increase towards the base of the coal.

GEOCHEMISTRY OF DGC SAMPLES

Based on analysis of the whole-coal and lithotype (non-DGC) ashes, Cs in the DGC-derived samples appears to be solely from the CsCl salt solutions used to prepare the DGC gradient. The PIXE geochemistry on the whole-coal basis was calculated on a Cs-free basis. The Cl content on the whole-coal basis was also adjusted stoichiometrically for Cs remaining from the DGC processing.

Cl and Br, both of which are best evaluated on the whole-coal basis, maximize in the vitrinite-rich separates.

In very-low ash samples such as these, organic sulfur is the most prevalent element other than C, H, N, and O. S and Cl trends for KCER-5445 are shown on Figure 2. On the whole-coal basis (pre-DGC), the sulfur content of KCER-5445 exceeds the ash content.

Ash-basis geochemistry is based on several assumptions: 1/ the "ash" percentage is 100% minus the "carbon" reported in the PIXE analysis ("carbon" includes all elements lighter than Na); 2/ most of the sulfur is organic and not part of the ash although organic sulfur can be fixed as sulfate in the low-temperature ashing process; and 3/ Cl and Br are volatilized, perhaps as HCl and HBr, in the ashing process.

Among the major elements, only P and Mg exhibit 10^2 order-of-magnitude ranges in concentration. In the case of Mg, the concentration peaks in the KCER-5445 >1.40 g/mL fractions. Ca and Mn are also relatively concentrated through this range, suggesting that the fusinite may be associated with a dolomite or magnesite with Mn substitution. Ca is also high in 5445 and 5447 1.22-1.30 g/mL fractions, but drops in the semifusinite-rich fractions. Fe is higher in 5445, peaking in the fractions above 1.31 g/mL. Siderite (FeCO_3), generally dispersed in vitrinite, is an important mineral phase in the Blue Gem.¹⁰ The Ca-Fe-Mg trends could be indicative of a shift in the dominant carbonate phase.

Si has a high concentration in the 5445 <1.12 g/mL fraction, perhaps representing biogenic silica, and in the pellets (material that exceeds the range of the density gradient) from the DGC runs. The Al variation is high in 5445 but somewhat muted in 5447 where DGC fraction 1 was not analyzed. K and the K/Al ratio minimizes in the vitrinite-rich fractions. K is also higher in 5447 than in 5445. Rb, which can substitute for K, only appears in the high-ash pellets.

P is exceptionally high in the 5445 1.18-1.22 g/mL fractions. The 1.20-1.22 g/mL fraction was analyzed for the other two coals but P was not significantly higher than in the other fractions.

On the ash basis, Ti maximizes in the high vitrinite fractions with 5447 having higher Ti concentration than 5445. Zr generally follows the Ti trends, peaking in the 5447 1.29-1.30 g/mL fraction at 6.5% (ash basis).

V maximizes in the high-vitrinite fractions, with 5447 having much higher concentrations, up to 14% in the 5447 1.29-1.30 g/mL fraction. In part, Cr follows the V trend, maximizing in the same fraction. Cr also has a high concentration in the 5445 1.12-1.15 g/mL fraction, corresponding to high concentrations of Ni, Cu, Mn, Zn, and Pb.

Ga, Ge, and Y peak in the lighter fractions and in the vitrinite-rich fractions and are higher in 5447 than in 5445. As and Se have greater concentrations in 5445 and peak in the lighter fractions and in the vitrinite-rich fractions. The highest concentration of As was found in the whole-lithotype ash of KCER-5443, a lithotype not processed by DGC. The As may be associated with pyrite in that high-sulfur lithotype.

Sr peaks in the vitrinite-rich fractions with similar trends and concentrations in each lithotype.

The elemental associations, or at least coincidences, noted are: Mg-Ca, Fe-Ca, and Mn-Ca; Ti-Zr; V-Cr; Cr-Ni-Cu-Mn-Zn-Pb (in a low-density split), Co-Ni, and Cu-Zn; Ga-Ge-Y; and As-Se. Of additional interest is the consistency of association of an element with a particular density split. Fraction 21, the high density "pellet" recovered from the rotor outer wall should contain minerals and associated elements not otherwise associated with macerals. Not surprisingly, elements clearly associated with mineral phases, such as Si and Al in clays, exhibit much higher concentrations in the pellet than in the lighter fractions. Many elements have somewhat mixed trends but Cl and Br are clearly higher in the organic-rich fractions than in the pellet. As, with Se showing an indeterminate trend, and Ga, with Ge showing an indeterminate trend, are higher in the organic-rich fractions. As noted above, Sr is one element which is consistently higher in the highest vitrinite fractions. Ca is also high through the vitrinite range although its peak is broader than the Sr peak. It is possible that Sr is closely associated with the carbonate phase of the vitrinite-rich fractions. Ga and Ge also tend to peak in the vitrinite-rich fractions.

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Table 1. Proximate analysis and maceral content of samples used in study.

KCER #	Ash (dry)	S _T (dry)	VM (dry)	Vit	Fus	Sfus	Mic	Ex	Res
5445	0.40	0.63	39.13	78.5	6.0	2.8	2.5	10.1	0.1
5447	1.47	0.61	37.03	77.6	7.2	3.6	2.7	8.7	0.2

Figure 1. Group maceral content of KCER-5445 vs. DGC fraction.

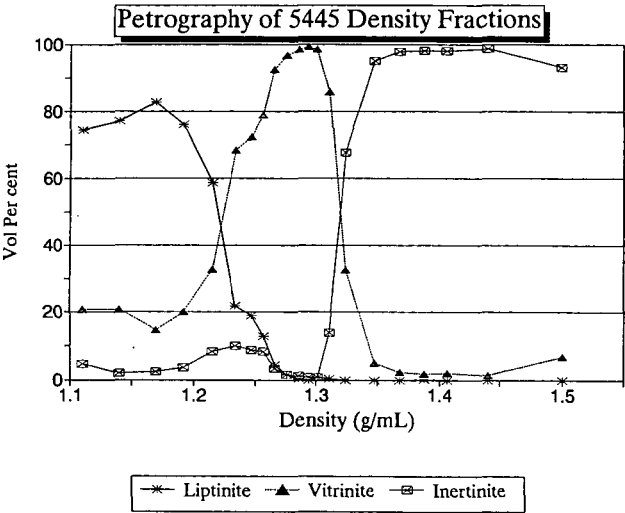


Figure 2. S_T and Cl of KCER-5445 vs. DGC fraction.

